# Deposition Phase Diagrams for Optimization of Thin Film Si:H and $Si_{1-x}Ge_x$:H

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NREL
National Renewable Energy Laboratory

# Outline:

1. Motivation
2. Background on interpretation:
   roughness evolution from RTSE
3. Experimental details:
   plasma-enhanced chemical vapor deposition (PECVD)
4. Summary of previous studies of Si:H:
   comparison of rf and vhf PECVD for high rate growth
5. Comparison of Si:H and $Si_{1-x}Ge_x$:H phase diagrams:
   standard deposition conditions
6. Comparison of $Si_{1-x}Ge_x$:H phase diagrams:
   effect of temperature
7. Comparison of Si:H and $Si_{1-x}Ge_x$:H phase diagrams:
   effect of electrode configuration
8. Summary and future directions

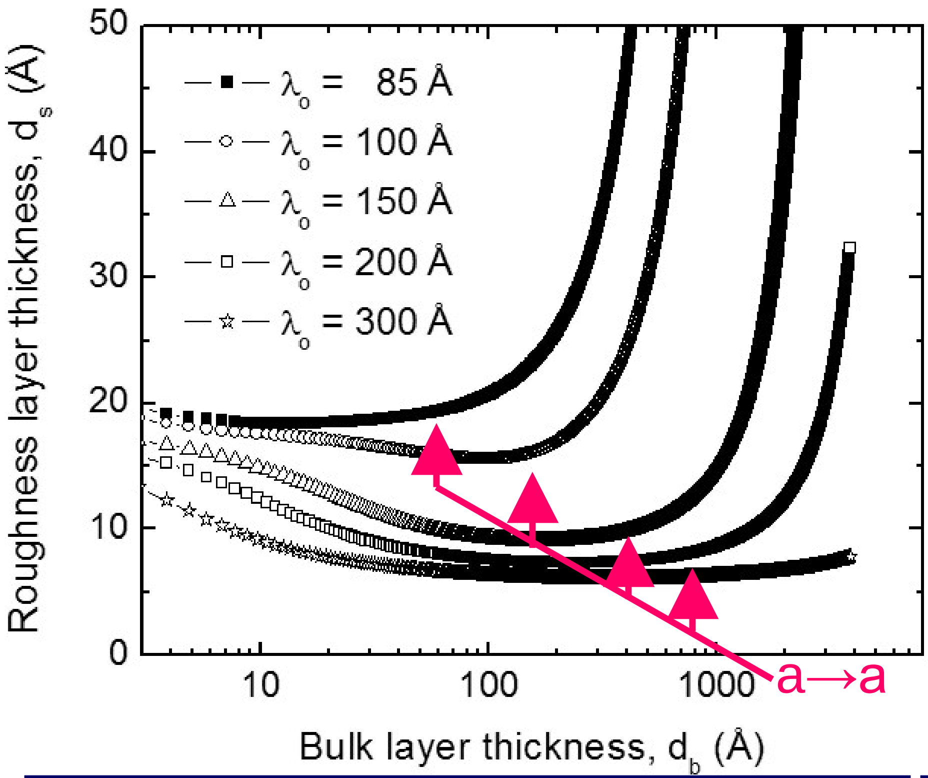
# 1. Motivation

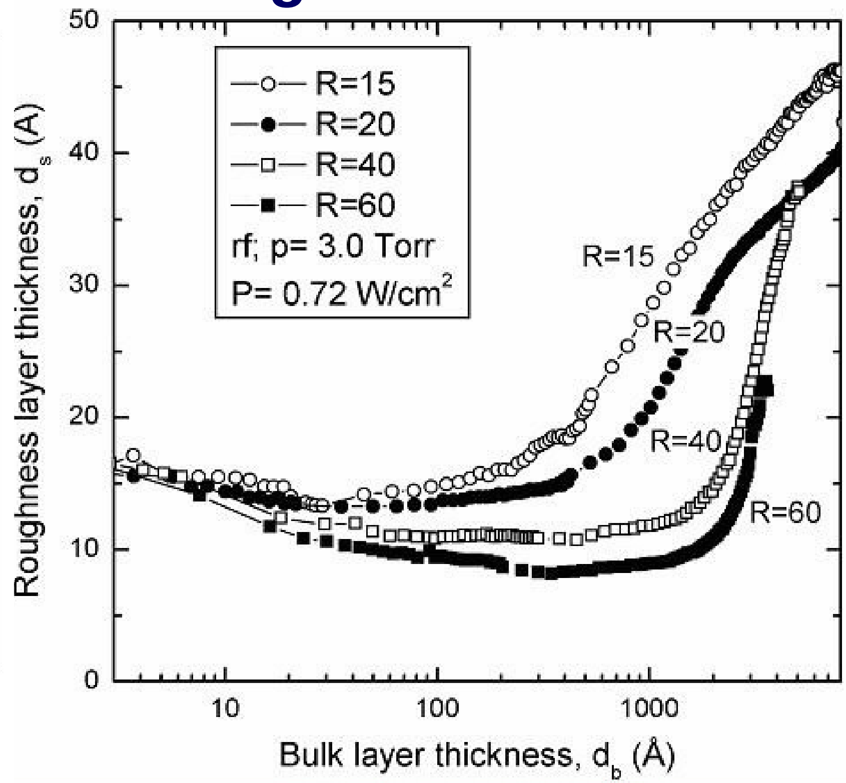
We seek to optimize the i-layer components of a-Si:H-based solar cells that apply triple junction n-i-p design based on a better understanding of the growth process achieved through deposition phase diagrams.

The primary deposition principle for the a-Si:H i-layer is to employ highest possible $H_2$ dilution level $R=[H_2]/[SiH_4]$ without crossing the (amorphous)-to-(mixed-phase) transition [a $\rightarrow$ (a+$\mu$c)].
Reason: *For any set of deposition conditions* increasing $H_2$-dilution improves ordering, decreases defects, and increases stability.

Another principle is to ensure the largest possible thickness for the onset of amorphous roughening transition [a $\rightarrow$ a] as assessed in studies on c-Si substrates.
Reason: The a $\rightarrow$ a transition is an indicator of surface diffusion which is enhanced when the surface defect density is reduced.

# 2. Background on interpretation: roughness evolution




Prediction of the surface roughness evolution (e.g., as would be measured by real time SE) for different values of the surface diffusion length $\lambda_0$

Experimental RTSE data obtained with $H_2$-dilution ratio R as the variable showing characteristics Similar to those of the models.

**Conclusion**

Increases in the thickness at which the a→a roughening transition occurs can be attributed to increases in the diffusion length of precursors on the a-Si:H surface.

# 3. Experimental Details: PECVD of a-Si:H and $Si_{1-x}Ge_x$:H for phase diagram development

- Same rf PECVD system used for all phase diagram studies
- Native oxide/c-Si substrates for smoothness and highest sensitivity to phase transitions

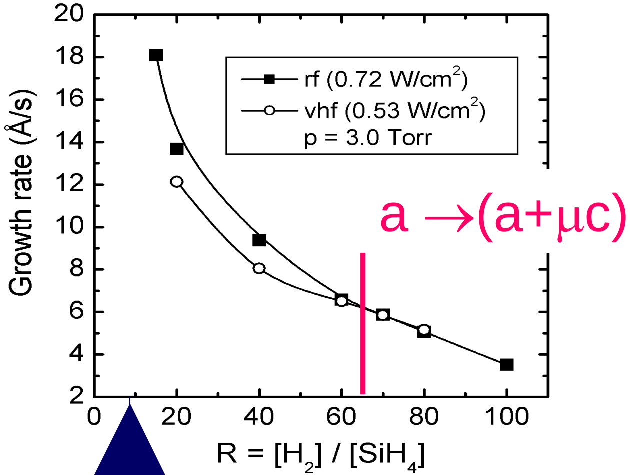
**Standard conditions (low rate)**

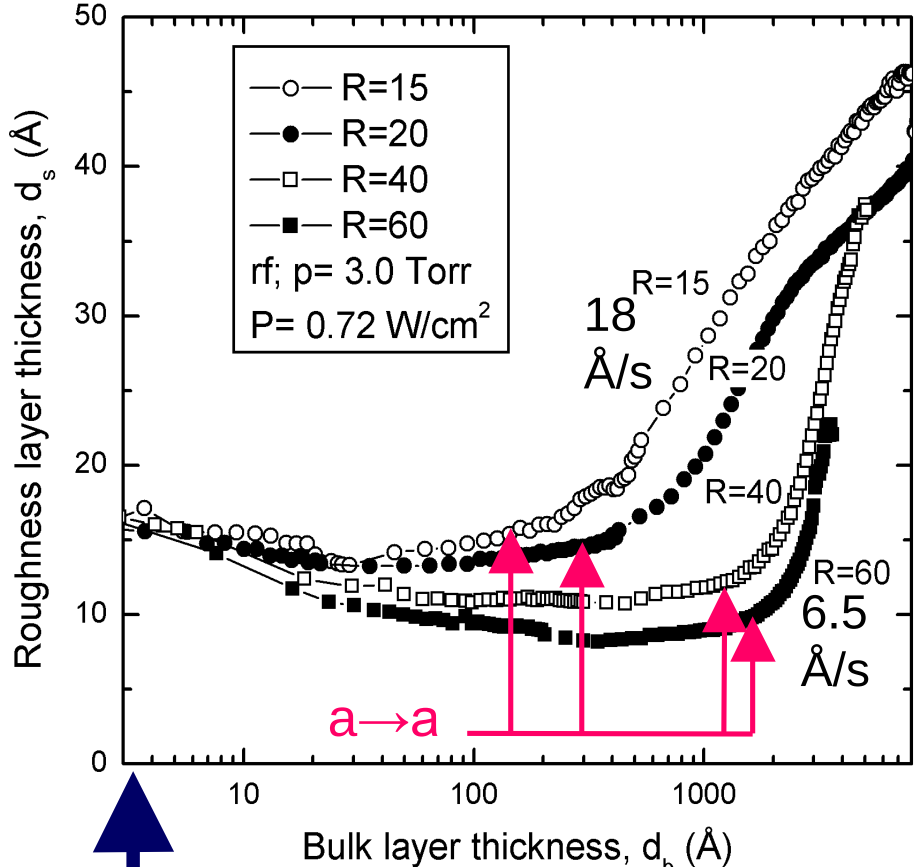
- Low temperature T=200°C
- Minimum rf plasma power for a stable plasma (0.08 $mW/cm^2$)
- Low partial pressure of source gases ($[SiH_4]+[GeH_4]$) (~0.06 Torr) with a total pressure < 1.0 Torr for all depositions versus $H_2$-dilution level
- Variable $H_2$ flow ratio, $R=[H_2]/\{[GeH_4]+[SiH_4]\}$ for the abscissa of the phase diagram to control the phase of the film (a, a+$\mu$c, $\mu$c)
- $GeH_4$ flow ratio, $G=[GeH_4]/\{[GeH_4]+[SiH_4]\}$
  - fixed at G = 0 for a room temperature optical gap of $E_g$~1.7-1.8 eV
  - fixed at G = 0.167 for a room temperature optical gap of $E_g$~1.3-1.4 eV

**Variable conditions for higher rate (a-Si:H) or improved quality (a-$Si_{1-x}Ge_x$:H)**

- Variable substrate temperature from 200$^o$C to 320$^o$C for optimization
- Variable power from 0.08 to 0.8 $mW/cm^2$ for higher rate
- Variable total pressure from 0.2 to 4 Torr for higher rate
- Variable plasma frequency 13.56 vs. 60 MHz for higher rate
- Anode (grounded) and cathode (–20 V self-bias) electrode configurations

## 4. Summary of previous studies of Si:H: comparison of rf and vhf plasma for high rate growth



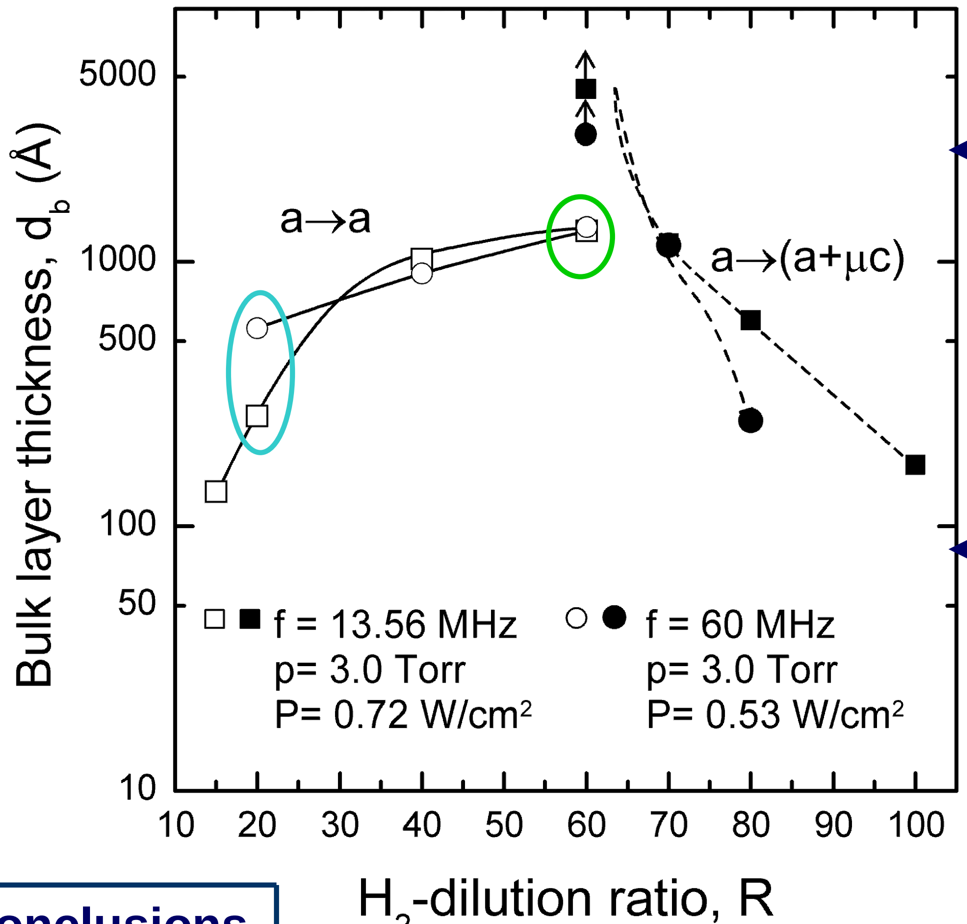




**Example:**
Elevated pressure to 3 Torr and power to (9 X standard) in rf PECVD yields 6.5 Å/s at the a → (a+μc) boundary

**Conclusion**

Under all elevated rate conditions that involve variations (increases) in:
(i) rf power; (ii) total gas pressure; and (iii) plasma frequency
the a-Si:H film structural evolution is improved with increasing R=[$H_2$]/[$SiH_4$]. Thus, process optimization by operation on the amorphous side of the a → (a+μc) boundary is a general principle irrespective of the deposition conditions.

# 4. Summary of previous studies of Si:H: comparison of rf and vhf plasma for high rate growth



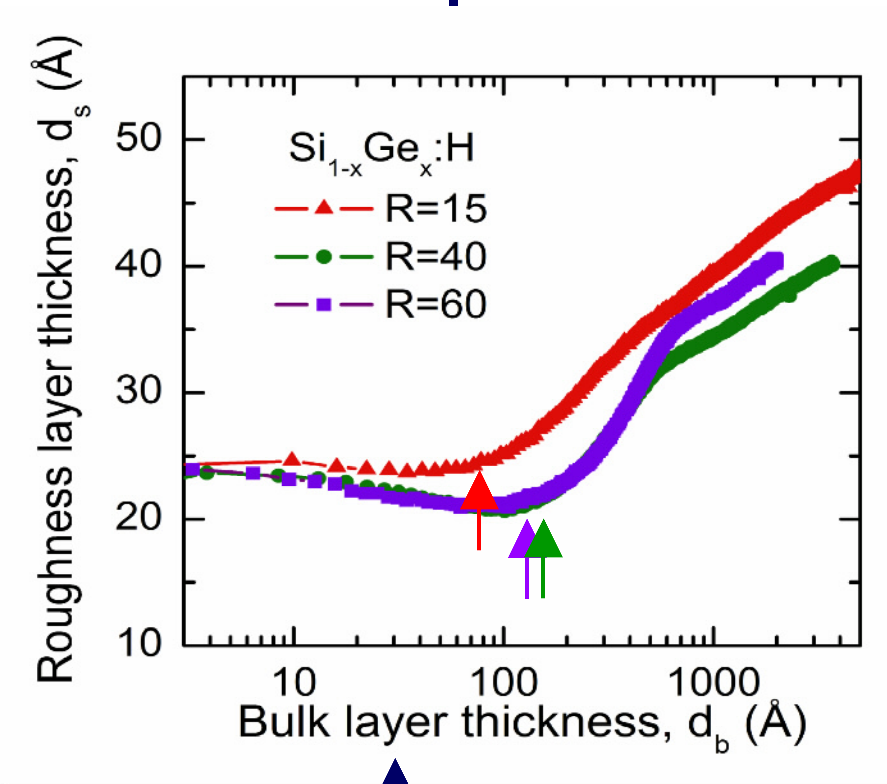

**Observations:**

- vhf yields similar $d_b$(a→a) and a-Si:H quality, under optimized conditions just before the a→(a+μc) boundary (R=60; rate 6.5 Å/s)
- vhf yields a larger $d_b$(a→a) and, thus, improved a-Si:H quality at R values much lower than the optimum (R=20; rate: ~13 Å/s)

**Conclusions**

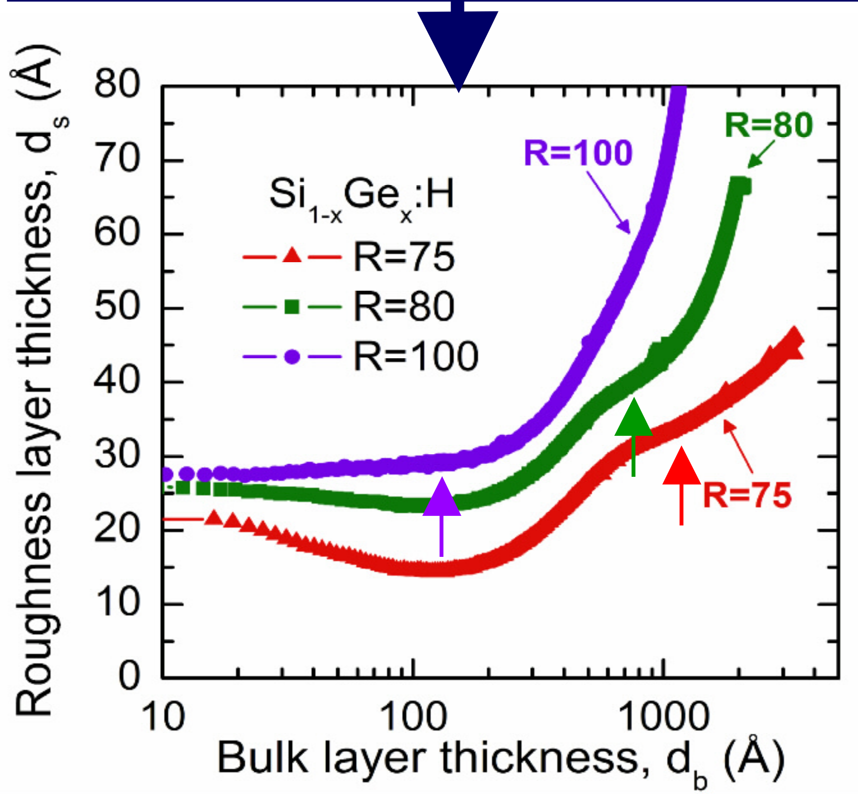
**For a-Si:H, vhf PECVD provides no significant advantage over rf PECVD under high deposition rate conditions when these conditions are optimized using variations in both R and gas pressure, and when identical deposition rates are ensured by using variations in plasma power.**

# 5. Comparison of Si:H and $Si_{1-x}Ge_x$:H phase diagrams: standard deposition conditions

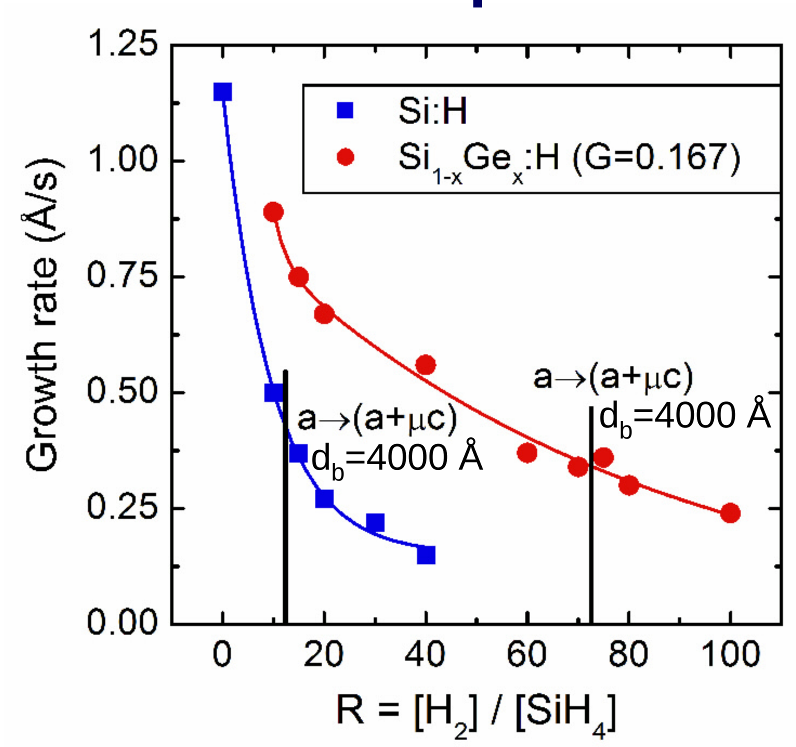



Evolution of roughness layer thickness for $Si_{1-x}Ge_x$ films with $R=[H_2]/\{[SiH_4]+[GeH_4]\} = 15, 40, 60$ that remain amorphous throughout; arrows indicate a → a transition

Evolution of roughness layer thickness for $Si_{1-x}Ge_x$ films with $R=[H_2]/\{[SiH_4]+[GeH_4]\} = 75, 80, 100$ that evolve from amorphous to (mixed-phase microcrystalline); arrows indicate a → (a+μc) transition



# 5. Comparison of Si:H and $Si_{1-x}Ge_x$:H phase diagrams: standard deposition conditions

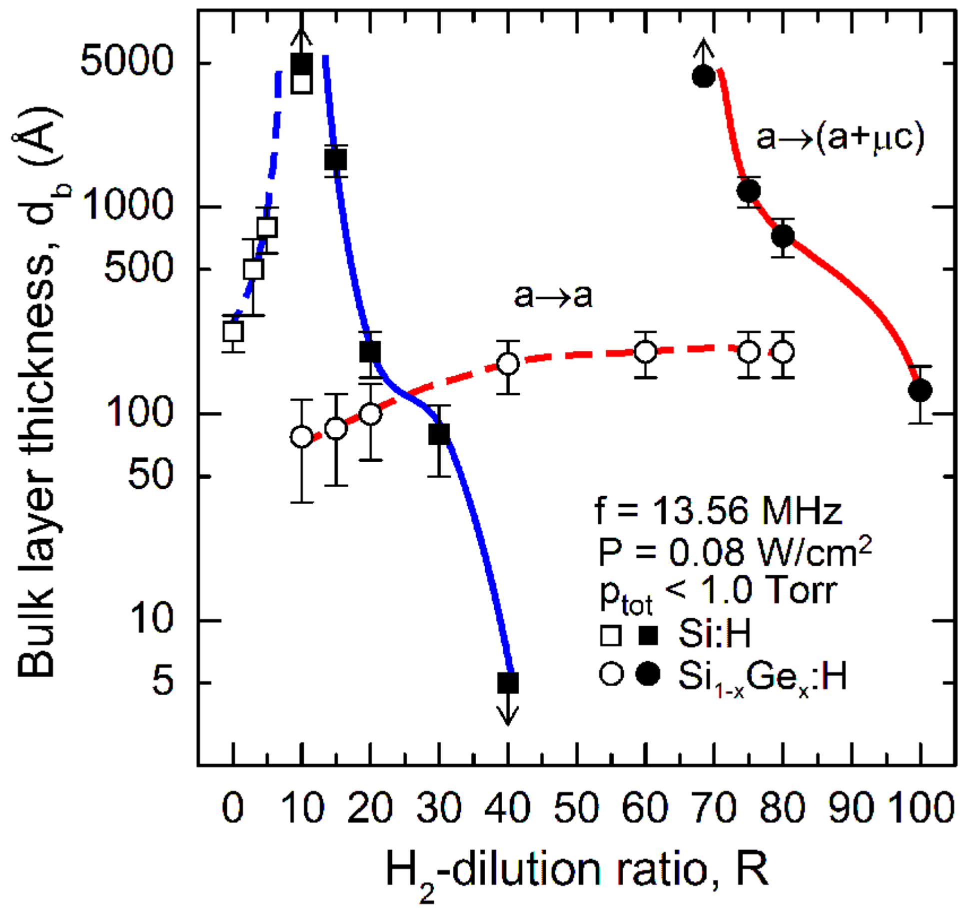



Higher deposition rates and a → (a+μc) transition thickness (at $d_b$=4000 Å) for $Si_{1-x}Ge_x$:H compared to Si:H prepared under similar conditions

For $Si_{1-x}Ge_x$:H compared to Si:H:

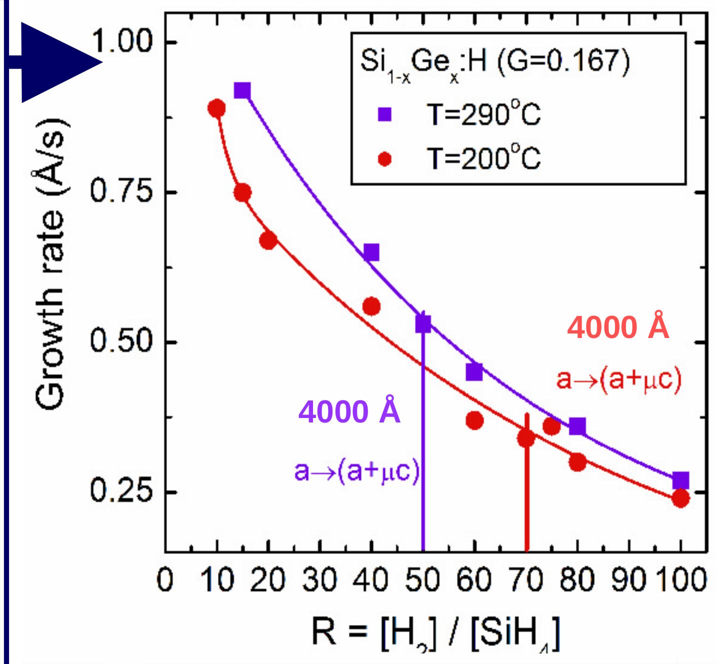
1) a → (a+μc) transition shifted to much higher R for all $d_b$

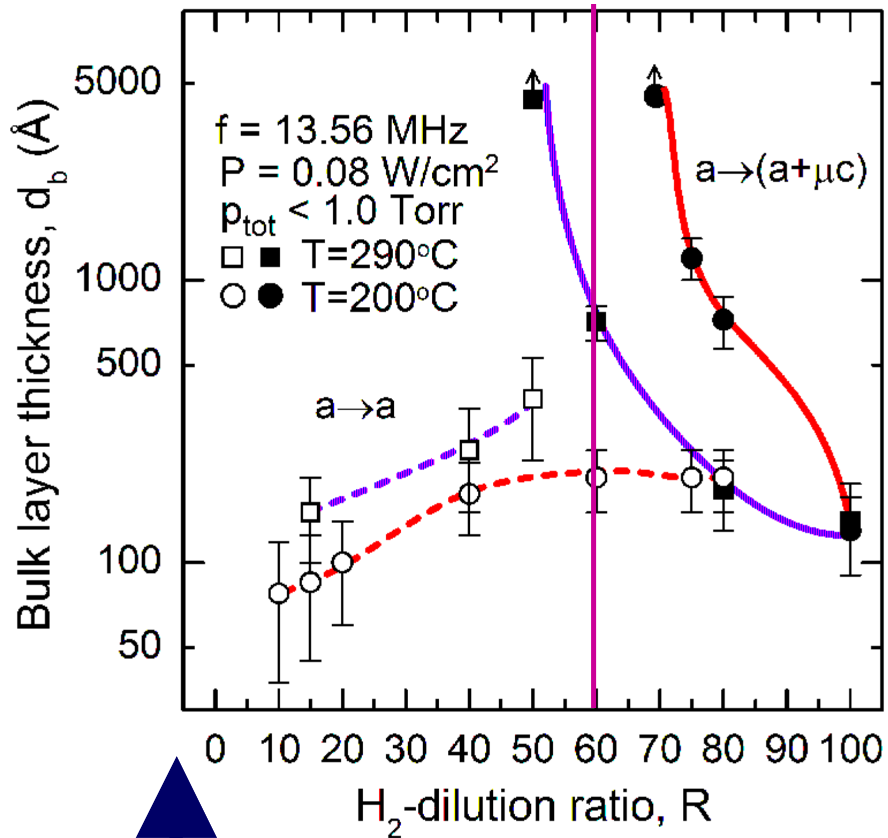
2) a → a transition saturates at a much lower bulk layer thickness $d_b$ < 200 Å



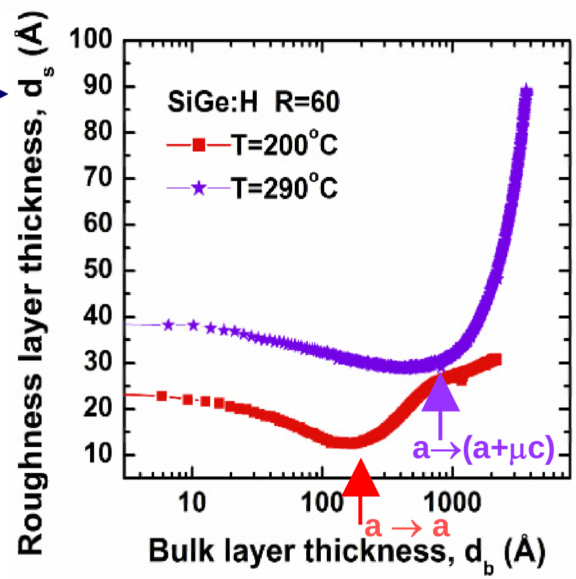
# 6. Comparison of $Si_{1-x}Ge_x$:H phase diagrams: effect of temperature

Increased deposition rate and decreased a → (a+μc) transition thickness (at $d_b$ = 4000 Å) with increase in T




Example: R=60 remains amorphous for T=200°C but exhibits a → (a+μc) transition for T=290°C

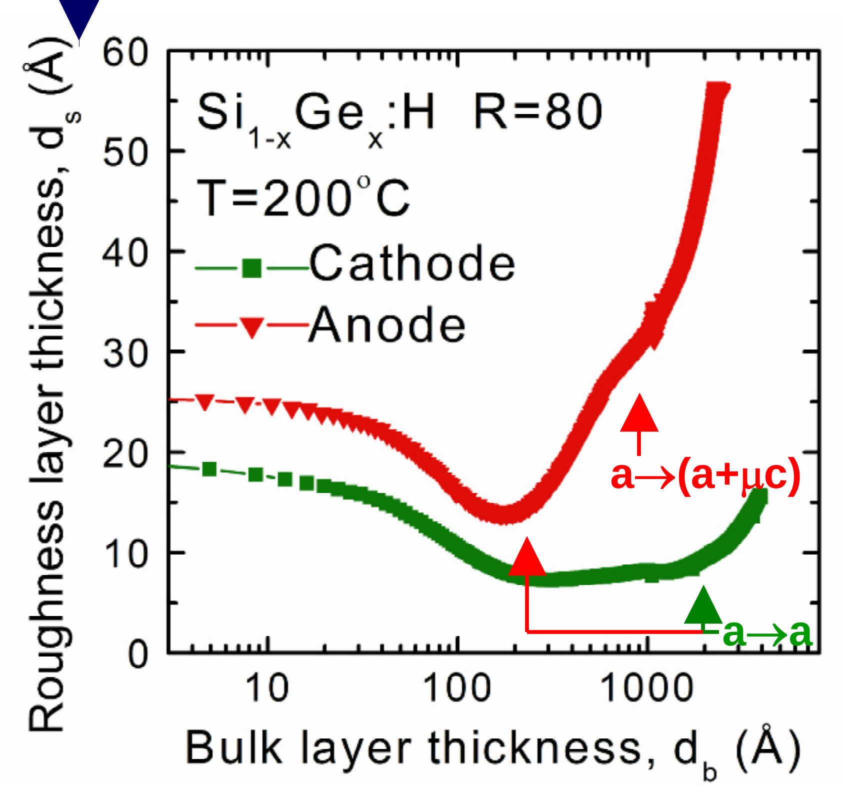


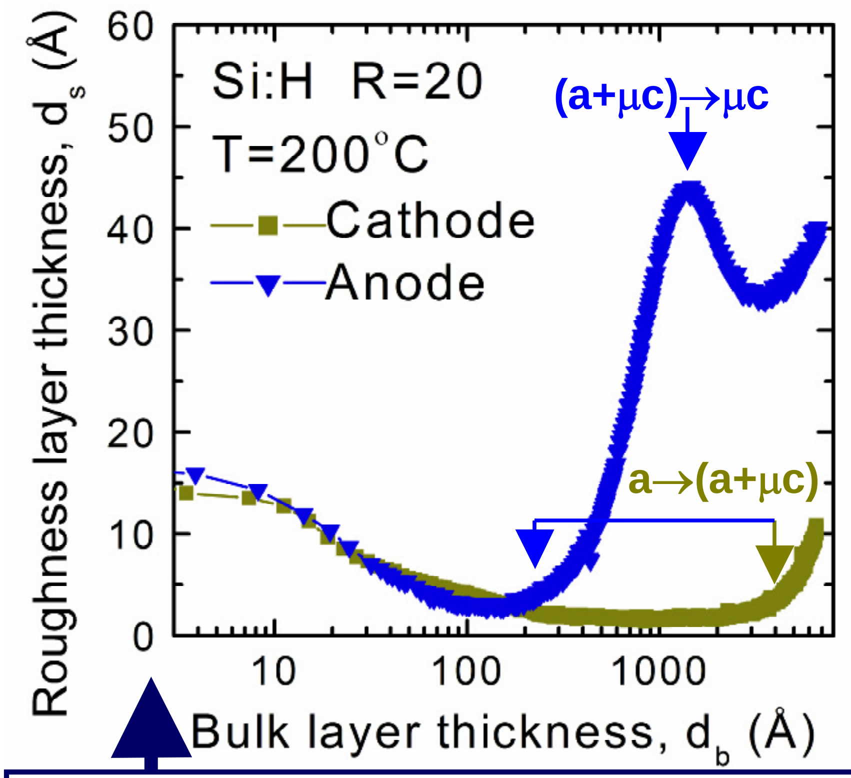

**Phase Diagram at T=290°C**

- Overall increase in a→a transition thickness for all R values
- Shift in a →(a+μc) transition boundary to lower R for all thicknesses
- Apparent modest improvement in material quality at the a → (a+μc) transition

# 7. Comparison of $Si:H$ and $Si_{1-x}Ge_x:H$ phase diagrams: effect of electrode configuration

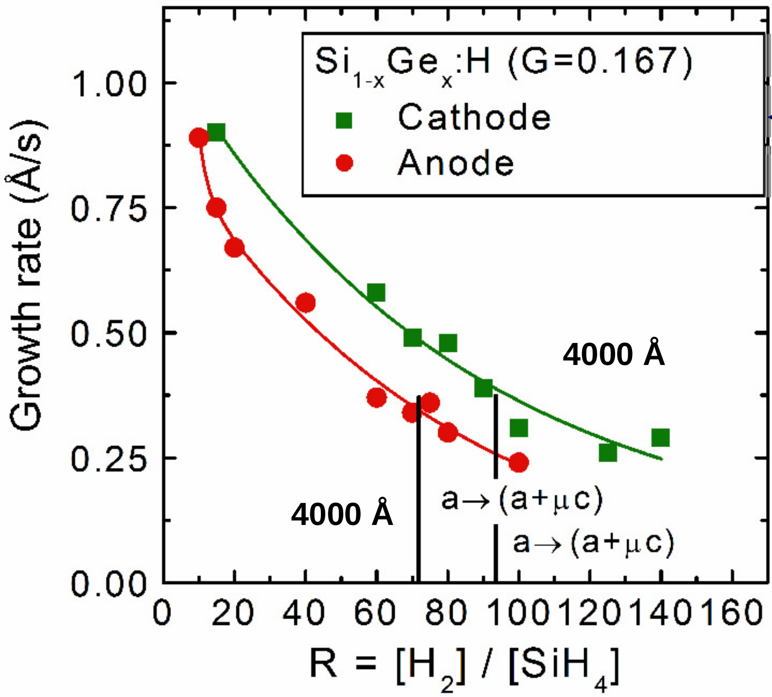
Comparison of the growth of R=80 $Si_{1-x}Ge_x:H$ films deposited on the anode and cathode.
For the deposition on the cathode:
- lower roughness amplitude
- a → a transition at much higher bulk layer thickness



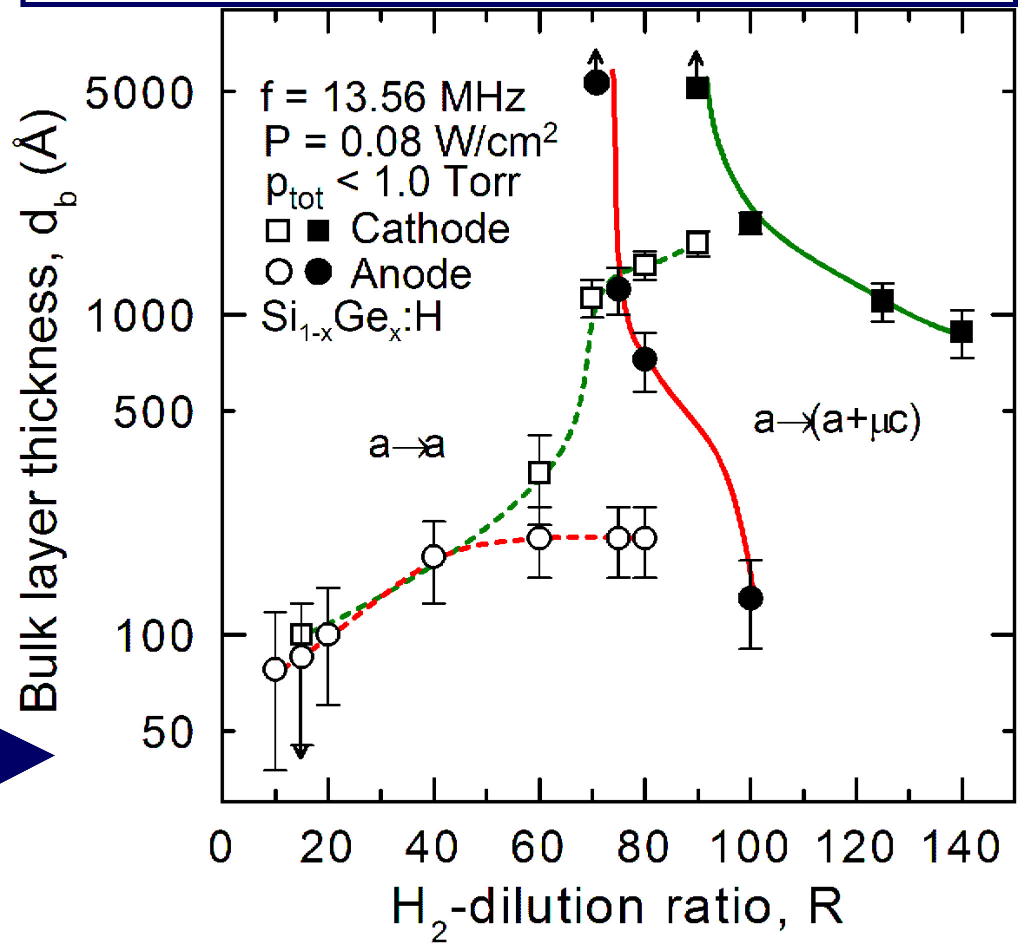

Comparison of the growth of R=20 $Si:H$ films deposited on the anode and cathode.
For the deposition on the cathode:
- lower roughness amplitude
- a → a transition at db > 3500 Å
- a → (a+μc) transition at much higher bulk layer thickness

# 7. Comparison of $Si_{1-x}Ge_x$:H phase diagrams: effect of electrode configuration

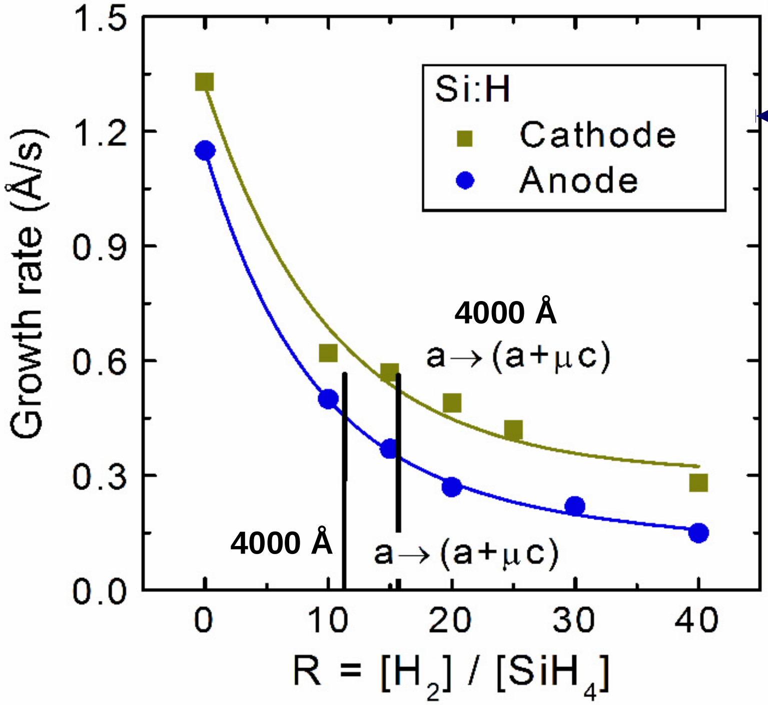



Higher deposition rates and higher a→(a+μc) transition thicknesses (at $d_b$ = 4000 Å) for $Si_{1-x}Ge_x$:H deposited at the cathode as compared to that deposited at the anode under otherwise similar conditions

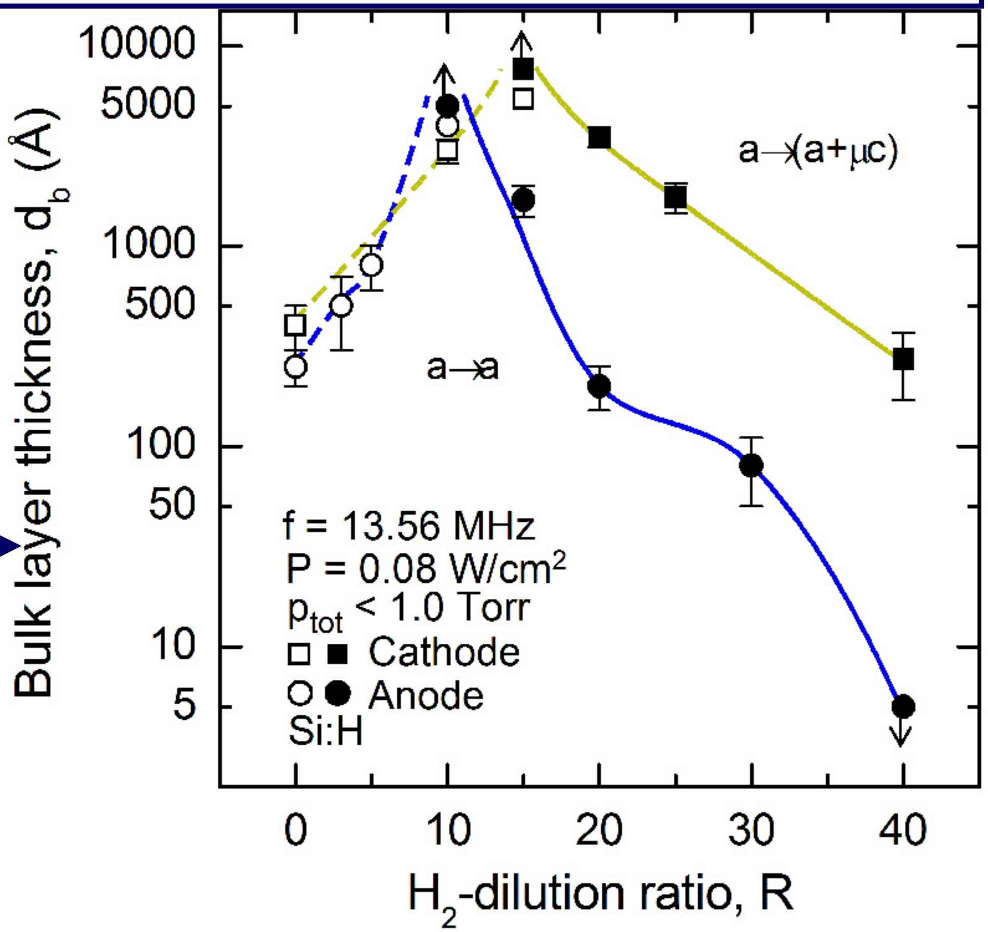
1) a → (a+μc) transition is shifted to much higher R for cathode $Si_{1-x}Ge_x$:H
2) This opens up a narrow window $70 \leq R \leq 90$ that allows the a → a transition to occur at a much higher $d_b$ value ~ 2000 Å for cathode $Si_{1-x}Ge_x$:H
   ⇒ very stable surfaces



# 7. Comparison of Si:H phase diagrams: effect of electrode configuration




Higher deposition rates and higher a→(a+μc) transition thickness (at $d_b$ = 4000 Å) for Si:H deposited at the cathode as compared with that deposited at the anode under otherwise similar conditions




1) a → (a+μc) transition shifted to higher R for cathode Si:H
2) This opens up a wider window $10 \leq R \leq 25$ that allows an *extended protocrystalline* regime for thicknesses at least to $d_b$ ~ 3000 Å
   ⇒ very stable surfaces

# Deposition Phase Diagrams for Optimization of Thin Film Si:H and $Si_{1-x}Ge_x$:H

## 8. Summary

**A.** For a-Si:H, vhf PECVD provides no significant advantage over rf PECVD under high deposition rate conditions when these conditions are optimized using variations in both R and gas pressure, and when identical deposition rates are ensured by using variations in plasma power. However, vhf PECVD does provide an advantage over rf when material quality is sacrificed for rate by backing away from the a $\rightarrow$ (a+μc) boundary.

**B.** A $Si_{1-x}Ge_x$:H phase diagram has been developed at T=200$^o$C under standard anodic deposition conditions and compared to the corresponding Si:H phase diagram. This comparison shows that:

1) the a→a transitions saturate at much lower $d_b$ for the alloys indicating an expected much lower quality
2) the a→(a+μc) transitions shift to higher R with alloying indicating a suppression of μc nucleation

## 8. Summary (continued)

**C.** A series of $Si_{1-x}Ge_x$:H phase diagrams have been developed over the range of temperatures (T=200 to 320°C). These diagrams show that:

1) the a → (a+μc) transitions shift to lower R with increasing T up to ~300°C
2) the a → a transitions shift weakly to higher bulk layer thickness with increasing T indicating modest improvements in the quality of the alloys

**D.** Si:H and $Si_{1-x}Ge_x$:H phase diagrams have been developed at T=200°C comparing the anode and cathode electrode configurations and the role of low-energy ion bombardment. These comparisons shows that:

1) the a → (a+μc) transitions shift to higher R when films are deposited on the cathode for both Si:H and $Si_{1-x}Ge_x$:H
2) a. for $Si_{1-x}Ge_x$:H a narrow window is opened leading to a→a transitions at much higher bulk thicknesses, suggesting significant improvements in material quality at the cathode

   b. for Si:H the a → (a+μc) transitions shift to higher bulk layer thicknesses, creating an extended protocrystalline regime at higher dilution levels, while maintaining a high a → a transition thicknesses at lower dilutions
3) the higher surface stability for cathodic films is accompanied by very smooth surfaces

## 8. Future Directions

- Reproduce cathodic film properties by biased deposition at the anode
- Explore additional non-standard deposition techniques to improve film quality and increase rate for cathode and biased anode deposition:
  - Temperature variation
  - Total pressure variation
  - Vhf plasma excitation frequencies

# Phase Diagrams for Optimization of Thin Film Si:H and $Si_{1-x}Ge_x$:H

## 8. Future Directions

- In collaboration with Prof. Xunming Deng, establish deposition phase diagrams for the three i-layers of the multijunction solar cell deposited in his laboratory

  In this study, vary:

  $H_2$ dilution level: $R=[H_2]/[SiH_4]$

  Germane content: $GeH_4/\{[Si_2H_6]+[GeH_4]\}$

  Ultimately establish multistep and graded layer processing directed by the phase diagrams that improve cell performance.

- Status: deposition chamber with window ports is under construction; new student in the process of training